HETEROGENEOUS REACTIONS OF OXIDES OF NITROGEN IN THE ATMOSPHERE: IS IT MAGIC?

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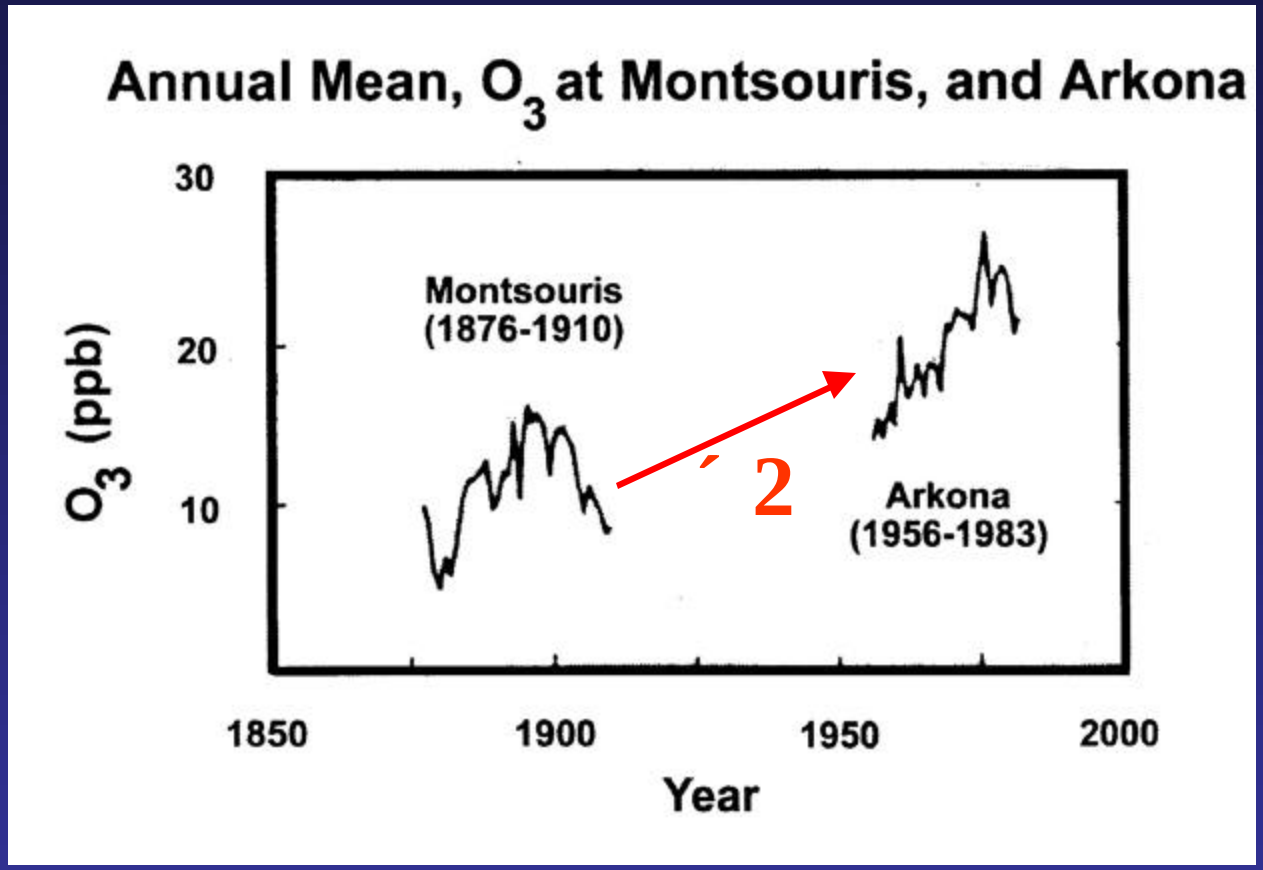
KEY ROLE OF OXIDES OF NITROGEN

- **Sole known anthropogenic source of ozone:**

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

$$O(^3P) + O_2 \rightarrow O_3$$

INCREASE IN GLOBAL O_3



- Attributed to increase in NO_x emissions

Volz & Kley, *Nature*, 332 240 (1988)

KEY ROLE OF OXIDES OF NITROGEN

- **Sole known anthropogenic source of ozone:**

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

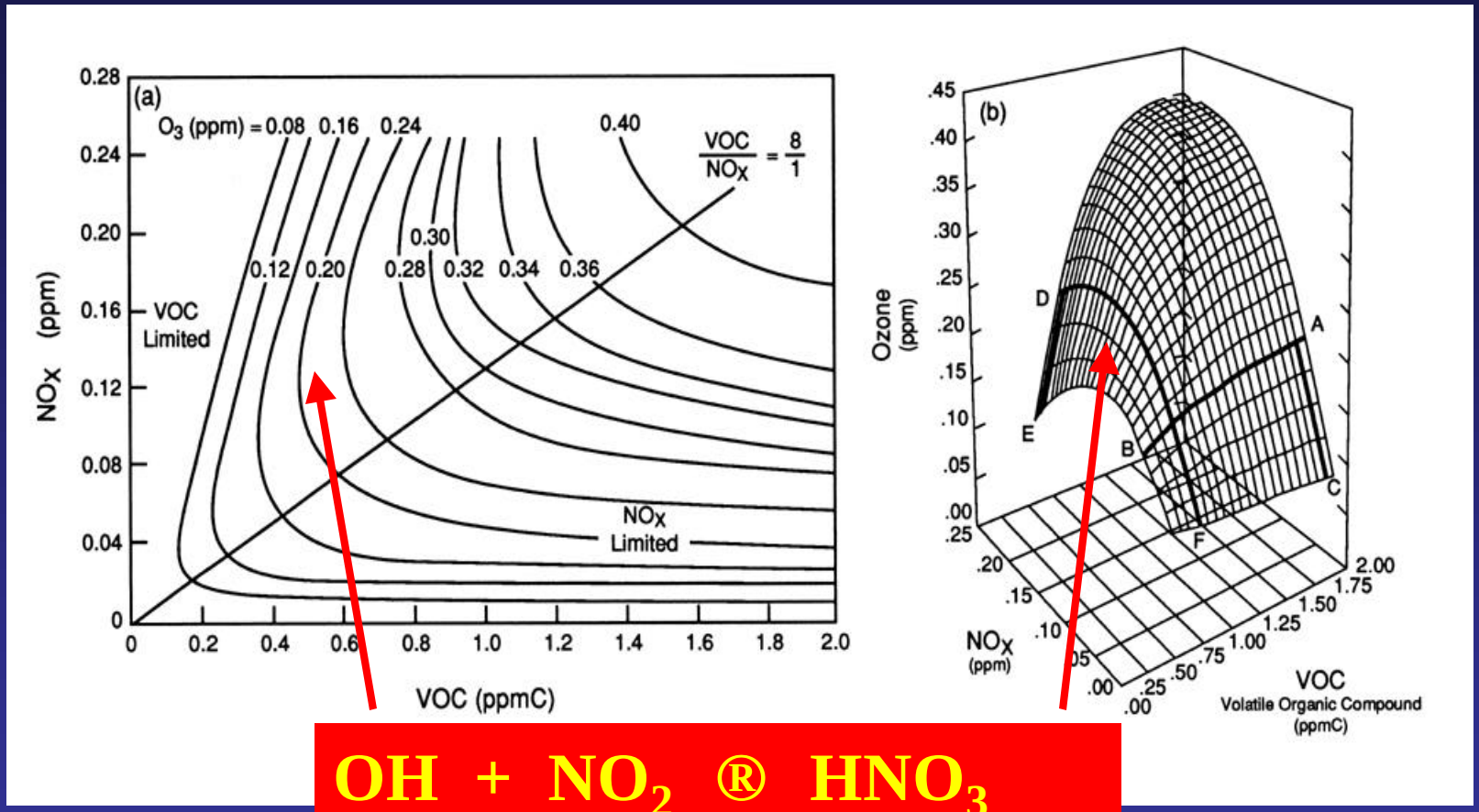
$$O(^3P) + O_2 \rightarrow O_3$$

- **Forms the nitrate radical (nighttime oxidations):**

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

- **Precursor to PAN, HNO_3, nitro-PAH etc.**

CONTROL STRATEGY PARADOX



$OH + NO_2 \rightarrow HNO_3$

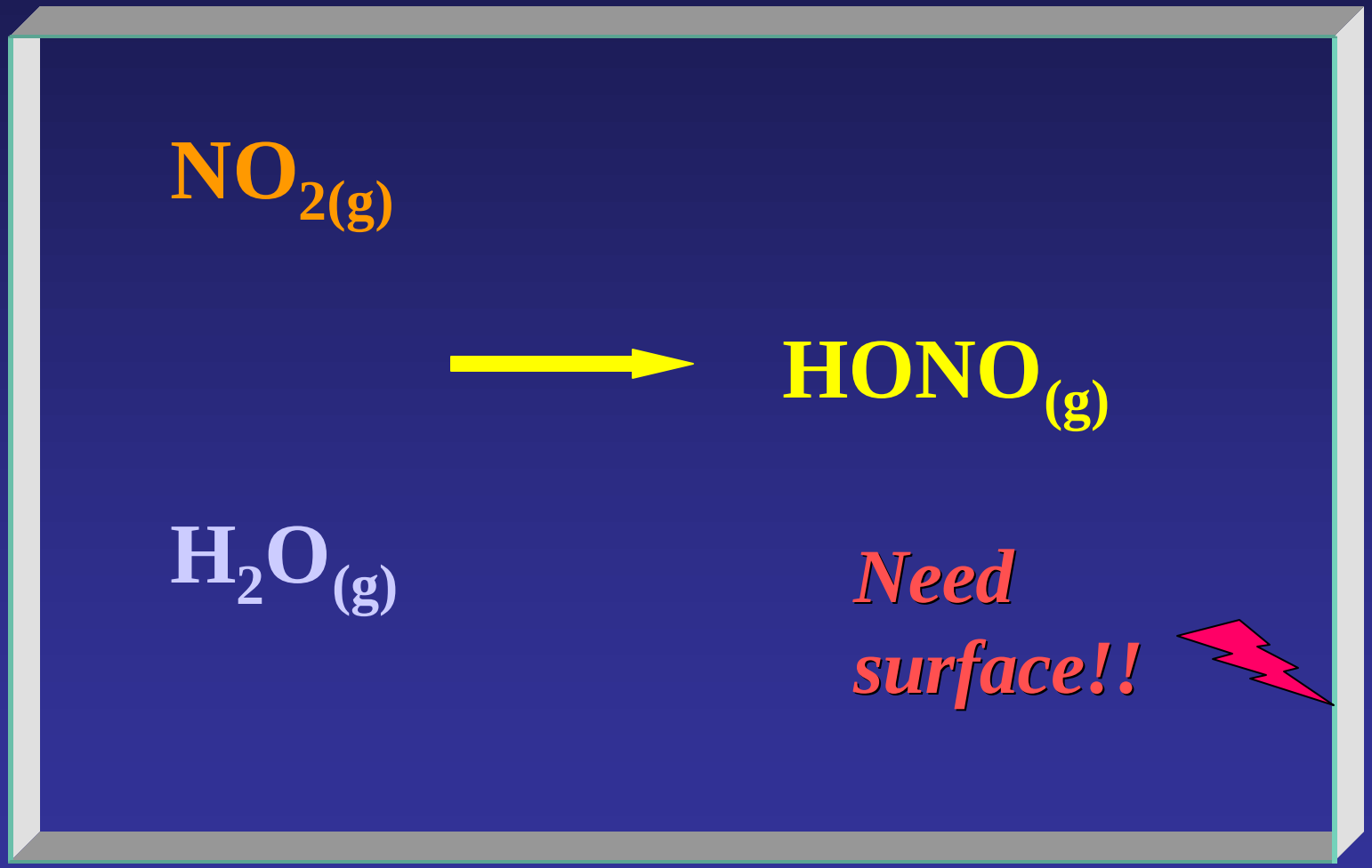
At low VOC/NO_x, O_3 predicted to decrease as NO_x increases.. BUT.. no heterogeneous chemistry!

NO_x CHEMISTRY

- Gas phase chemistry “relatively” well understood

- ***Heterogeneous chemistry????***

NO_x HETEROGENEOUS CHEMISTRY



OVERALL NO_2 HYDROLYSIS REACTION

"surface"

$$2\,NO_2 + H_2O \longrightarrow HONO + HNO_3$$

Never seen in gas phase!

OVERALL NO_2 HYDROLYSIS REACTION

magic

$$2\,NO_2 + H_2O \longrightarrow HONO + HNO_3$$

OTHER POTENTIAL HETEROGENEOUS NO_X CHEMISTRY ??

$HNO_{3\,(surface)} + NO_{(g)} \rightarrow HONO, NO_2$, others?

- suggested by Fairbrother et al. (1997)

"renoxification"

WHY IS HONO IMPORTANT?

- **Initiates VOC oxidation:**

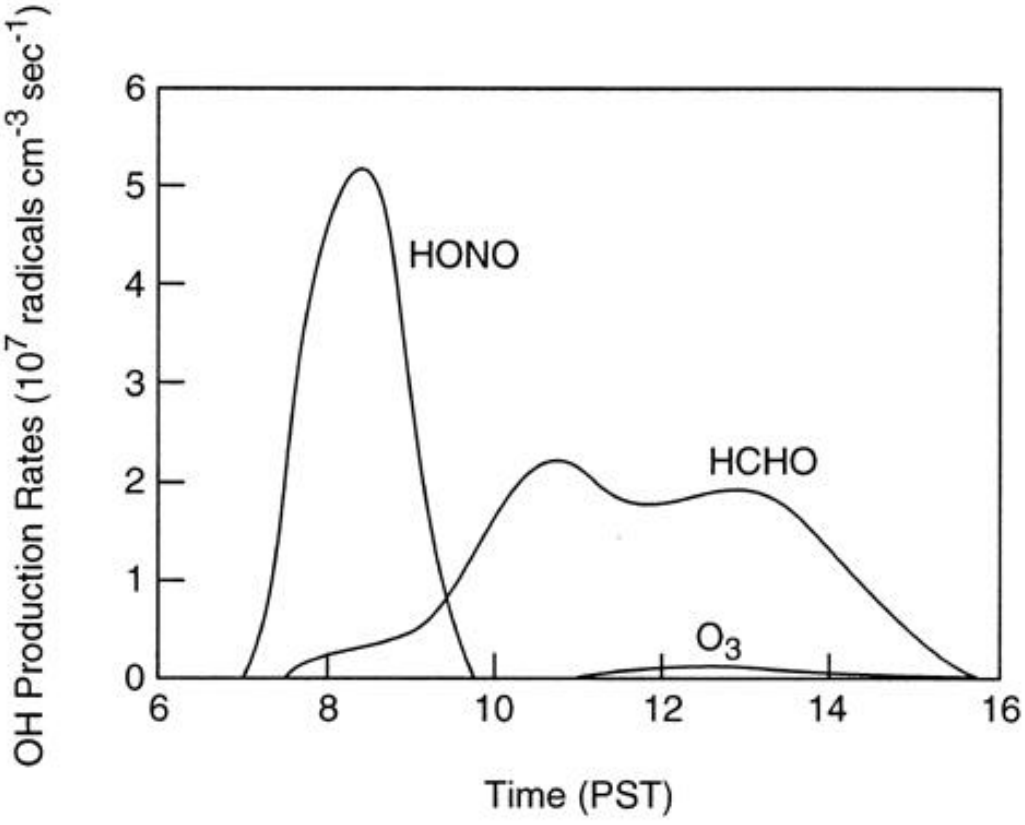
HONO + hu ® OH + NO

OH + VOC ® ® RO_2 → RO

NO **NO_2**

HOW IMPORTANT IS HONO?

Long Beach, CA, December 10, 1987



- **44 % of OH production over 24 hrs**

Winer & Biermann, *Res. Chem. Int.* 20 423 (1994)

SO WHAT??

- **"Pulse" of OH in early morning speeds up VOC oxidation and NO ® NO_2 ® O_3**

- **May move position of O_3 peak upwind and change peak level**

KNOWN SOURCES OF HONO

- **Direct emissions from non-catalyst equipped vehicles (e.g. Pitts et al, 1984; Wiesen et al, 2001)**

  - most cars have catalysts

- **OH + NO « HONO**

  - daytime when HONO photolyzes

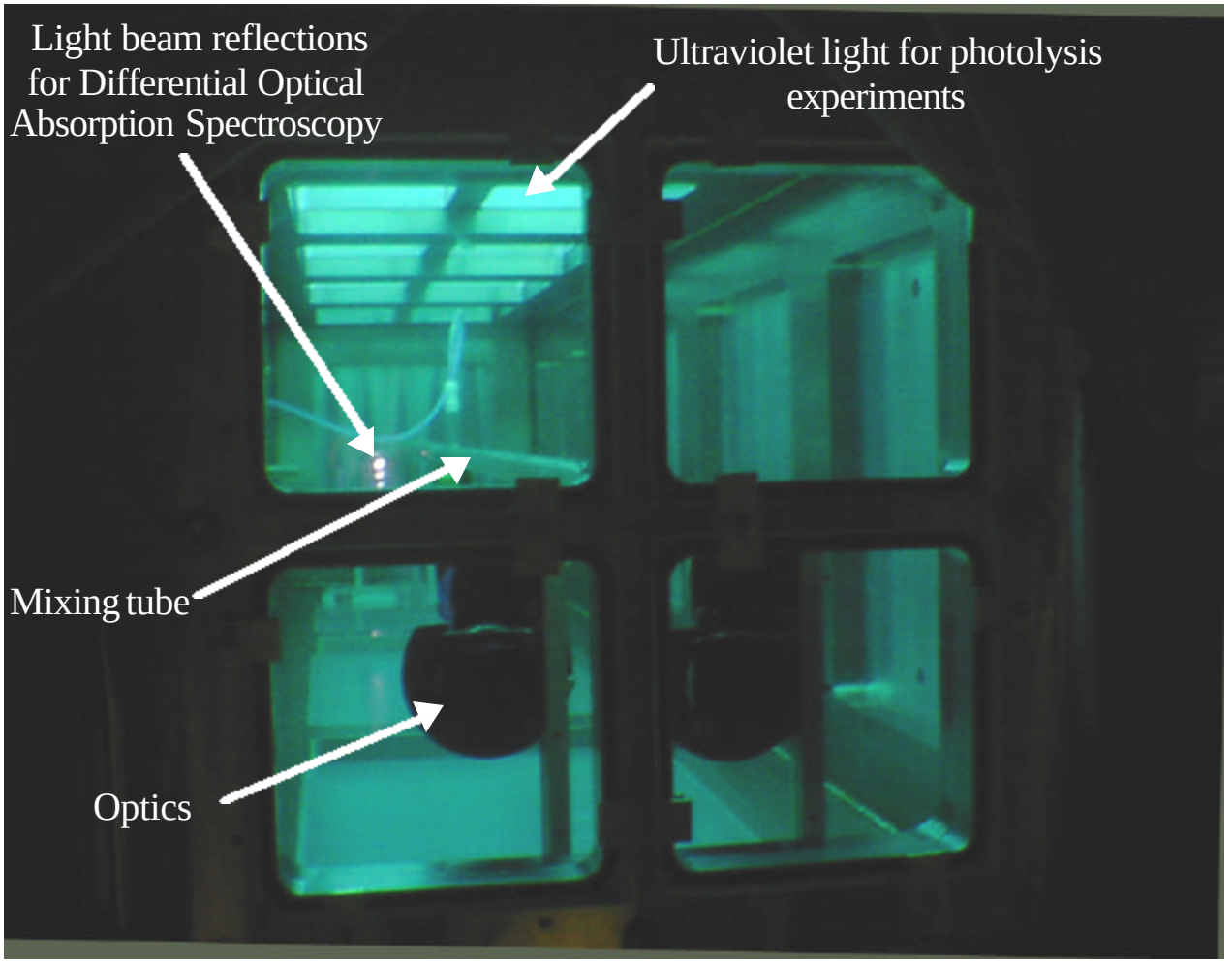
- **NO_2 + soot ® HONO**

  - surface deactivation of soot

OVERALL NO_2 HYDROLYSIS REACTION

"surface"

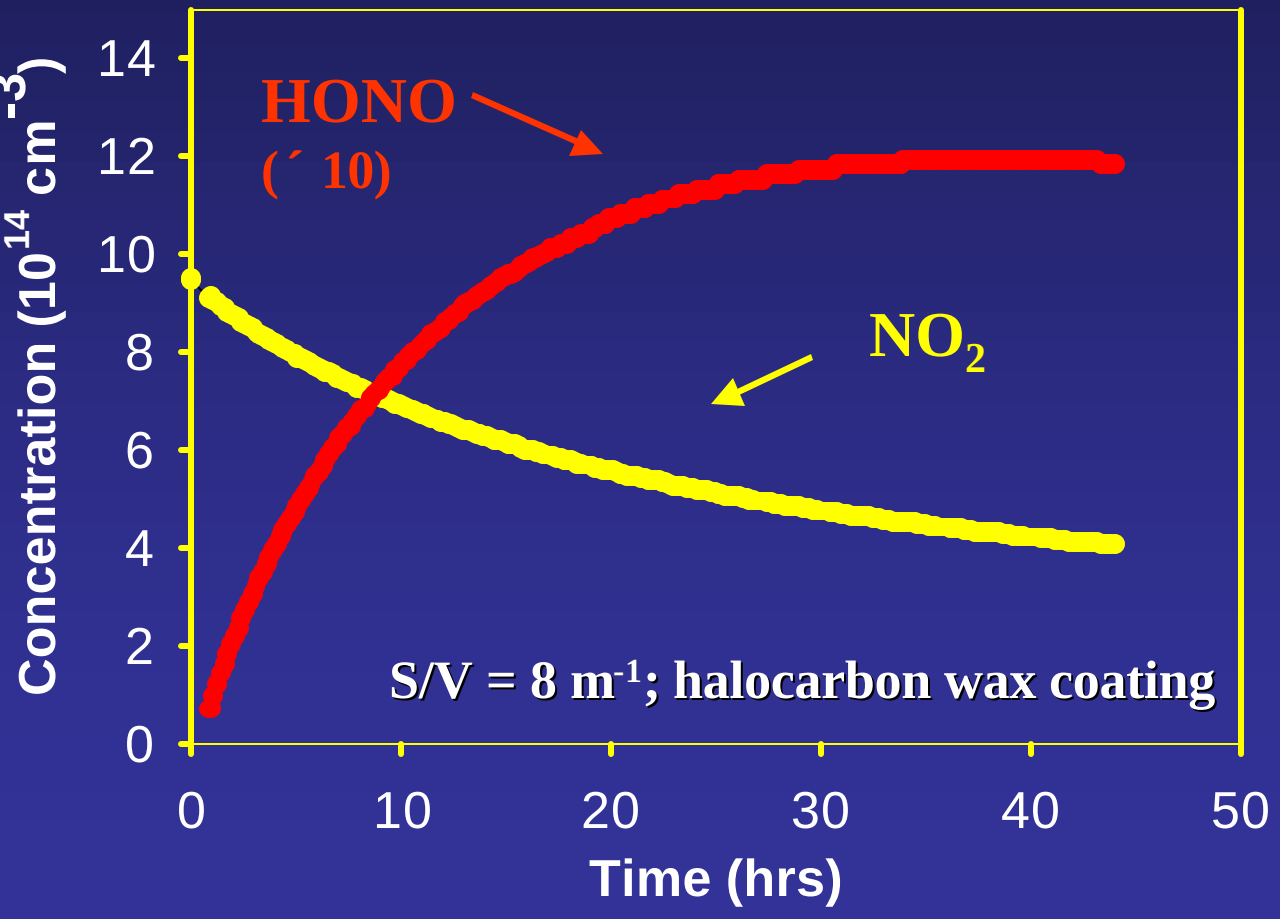
Aerosol Chamber



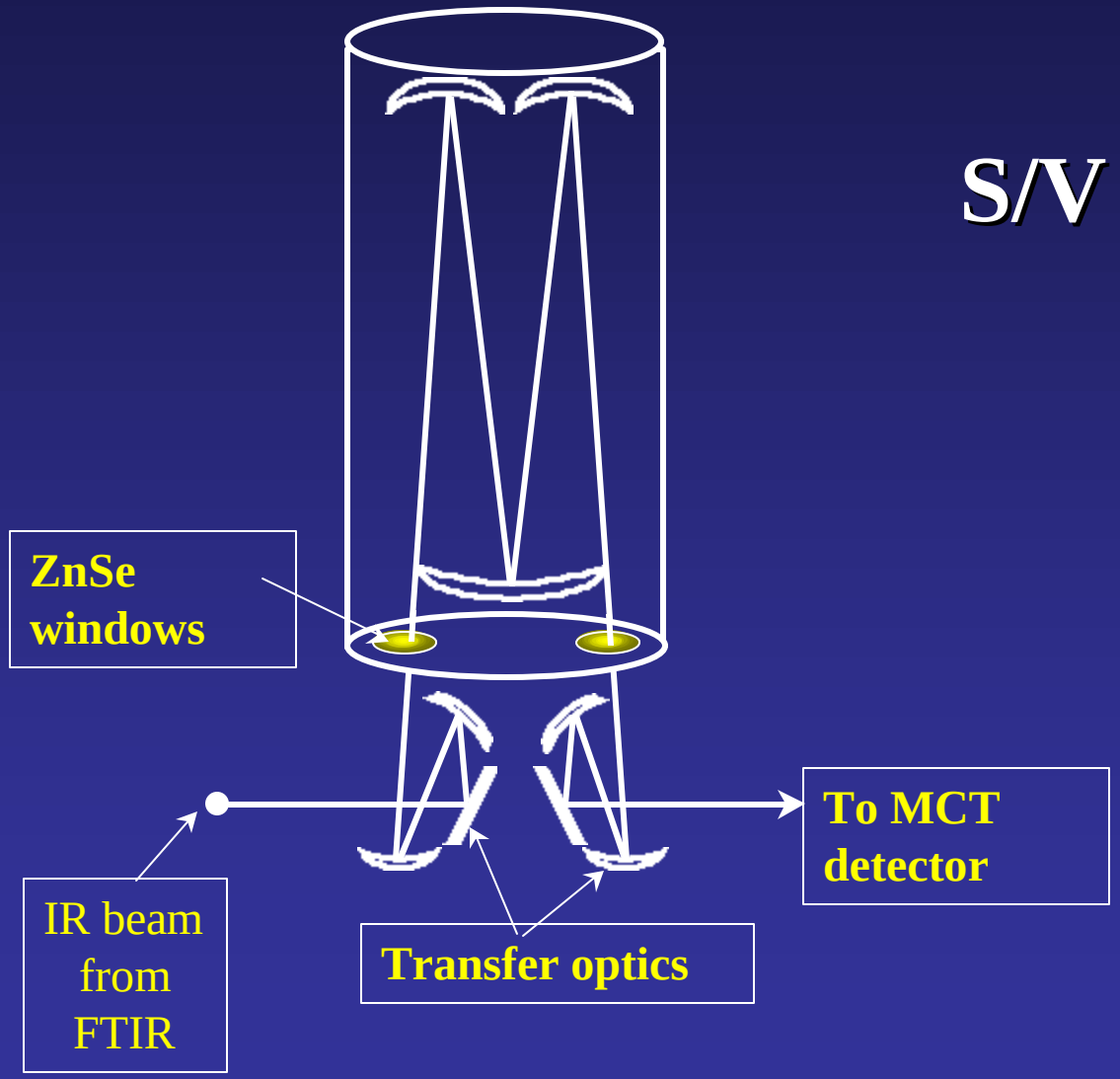
- Hydrolysis of NO_2 and Formation of HONO in the Presence of Aerosol

NO_2 HYDROLYSIS IN 561 L CHAMBER

85% RH; no aerosol present

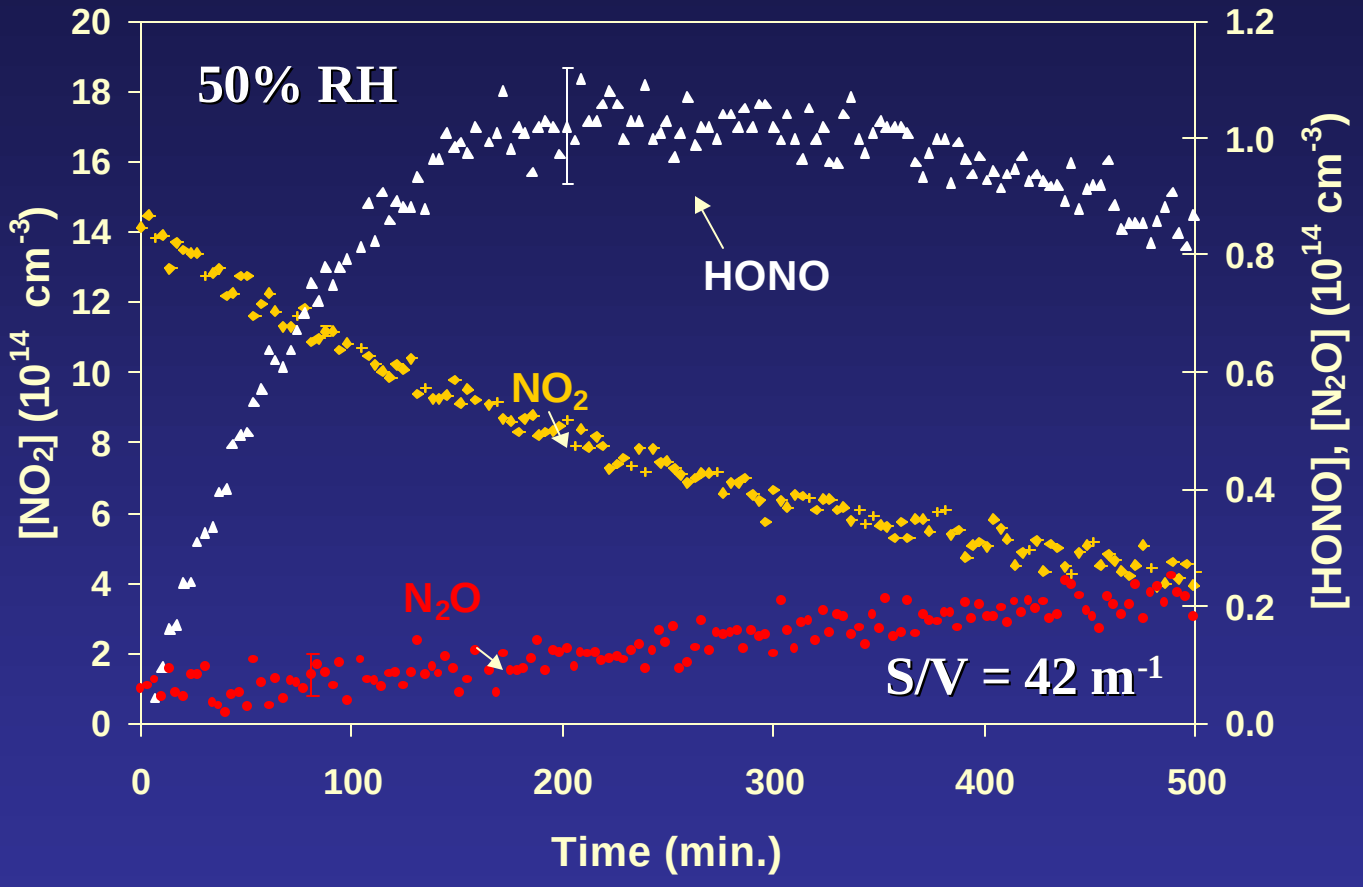


BOROSILICATE GLASS CELL (7 L)



$S/V = 42\ m^{-1}$

NO_2 HYDROLYSIS IN 7 L GLASS CHAMBER



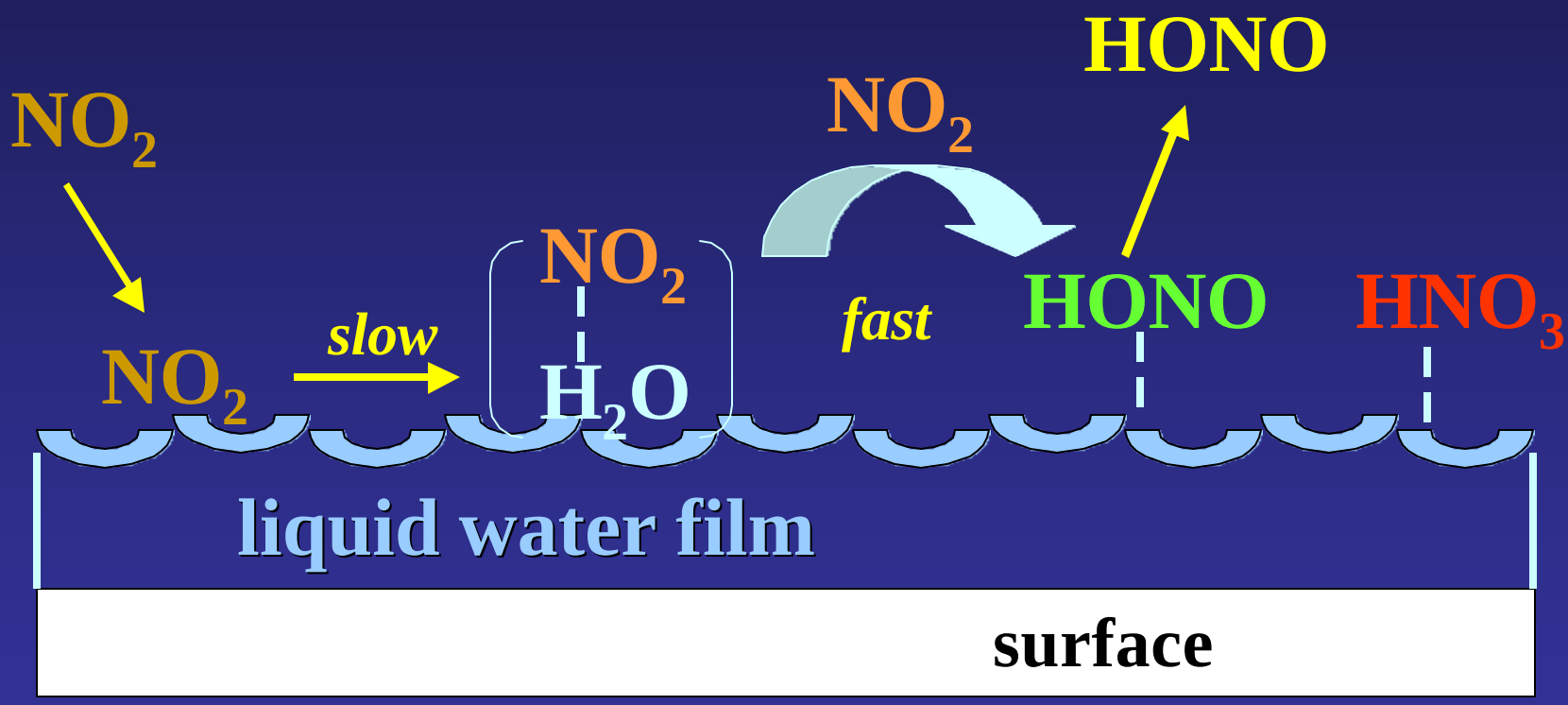
- Much faster HONO formation, with loss indicating secondary reactions
- N_2O and NO (not shown) are observed® from HONO??

SOME PREVIOUS OBSERVATIONS

- First order in NO_2, first order in H_2O
- HONO yields $\leq$ 50%
- HNO_3 not seen in gas phase
- No effect of underlying surface (glass, Teflon etc.)

England & Corcoran, 1974; *ten Brink et al*, 1978; *Sakamaki et al.*, 1983; *Pitts et al.*, 1984, 1985; *Akimoto et al.*, 1987; *Svensson et al.*, 1987; *Jenkin et al.*, 1988; *Wiesen et al.*, 1995; *Kleffman et al.*, 1998a,b; *Harrison & Collins*, 1998.

PITTS et al. MECHANISM FOR NO_2 HYDROLYSIS ON SURFACES



Pitts et al., *Int. J. Chem. Kinet.* 16 919 (1984)

UNANSWERED QUESTIONS

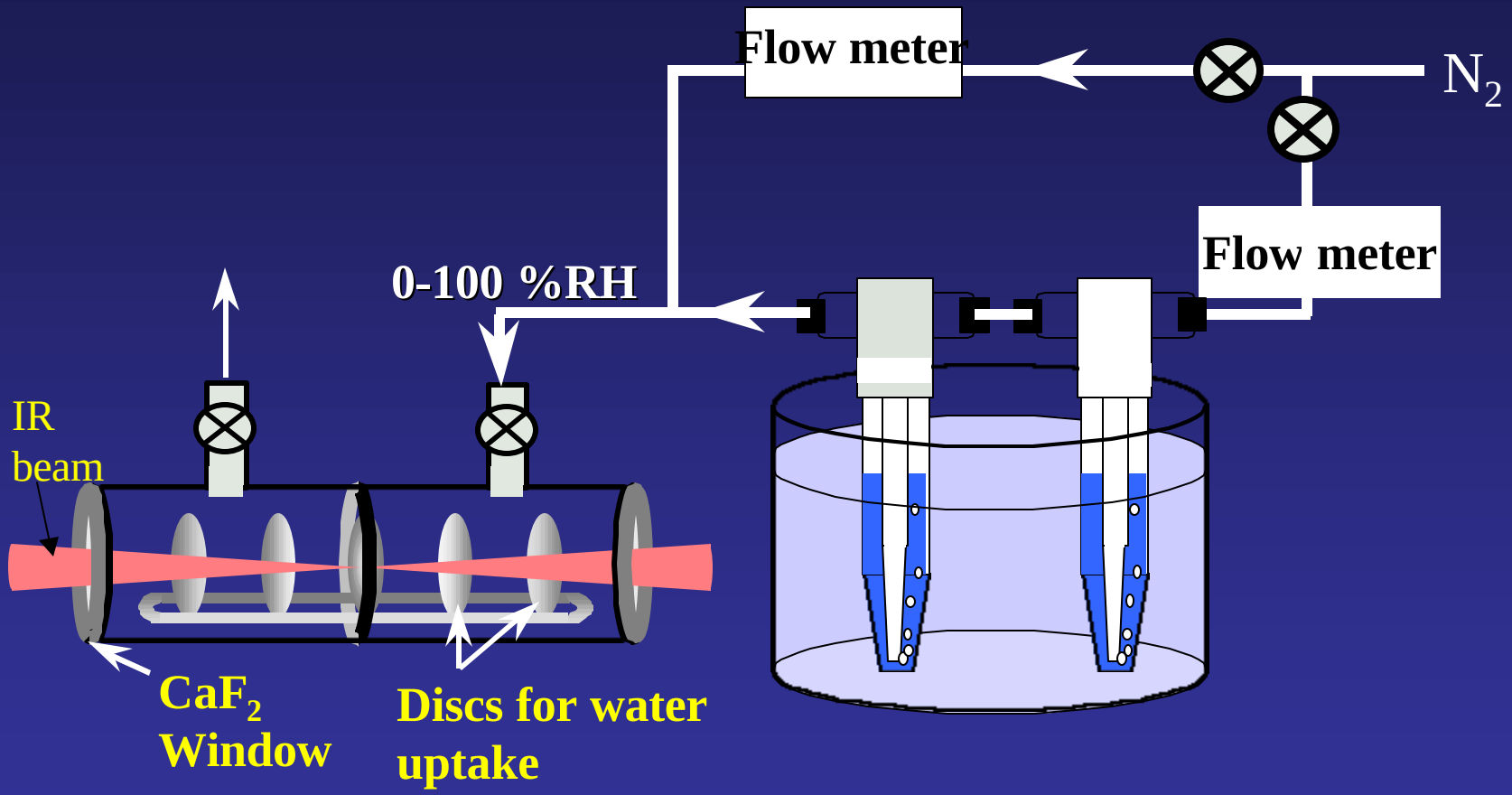
- What does “surface” mean?
- Is the water on the surface bulk liquid?
- How can laboratory studies be extrapolated to ambient conditions?

Need to know fundamental mechanism and kinetics!

NO_2 INTERACTIONS WITH WATER ON SURFACES

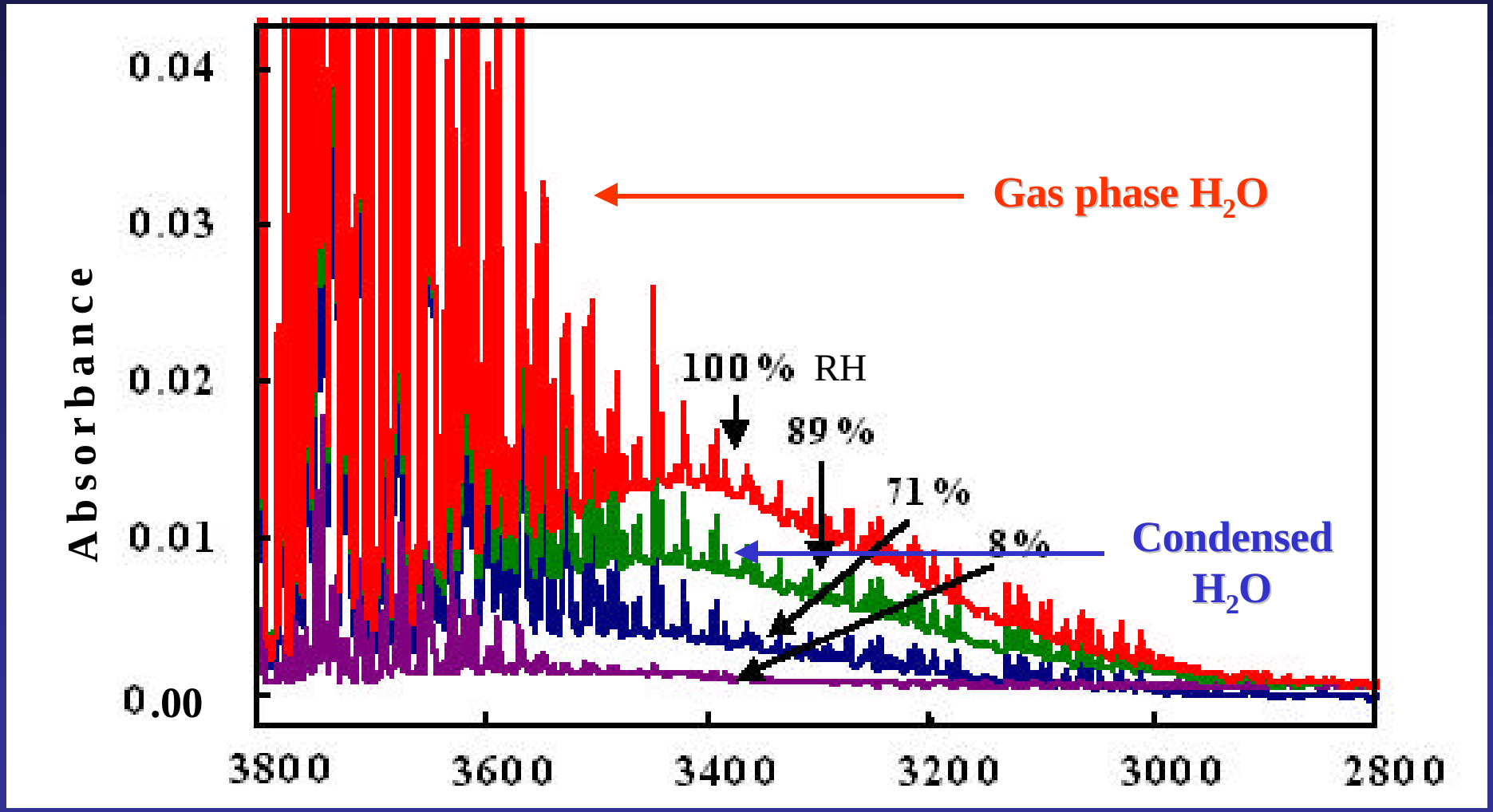
- How much water is on surfaces?
- Is it “bulk” water?

MEASUREMENT OF WATER ON SURFACES

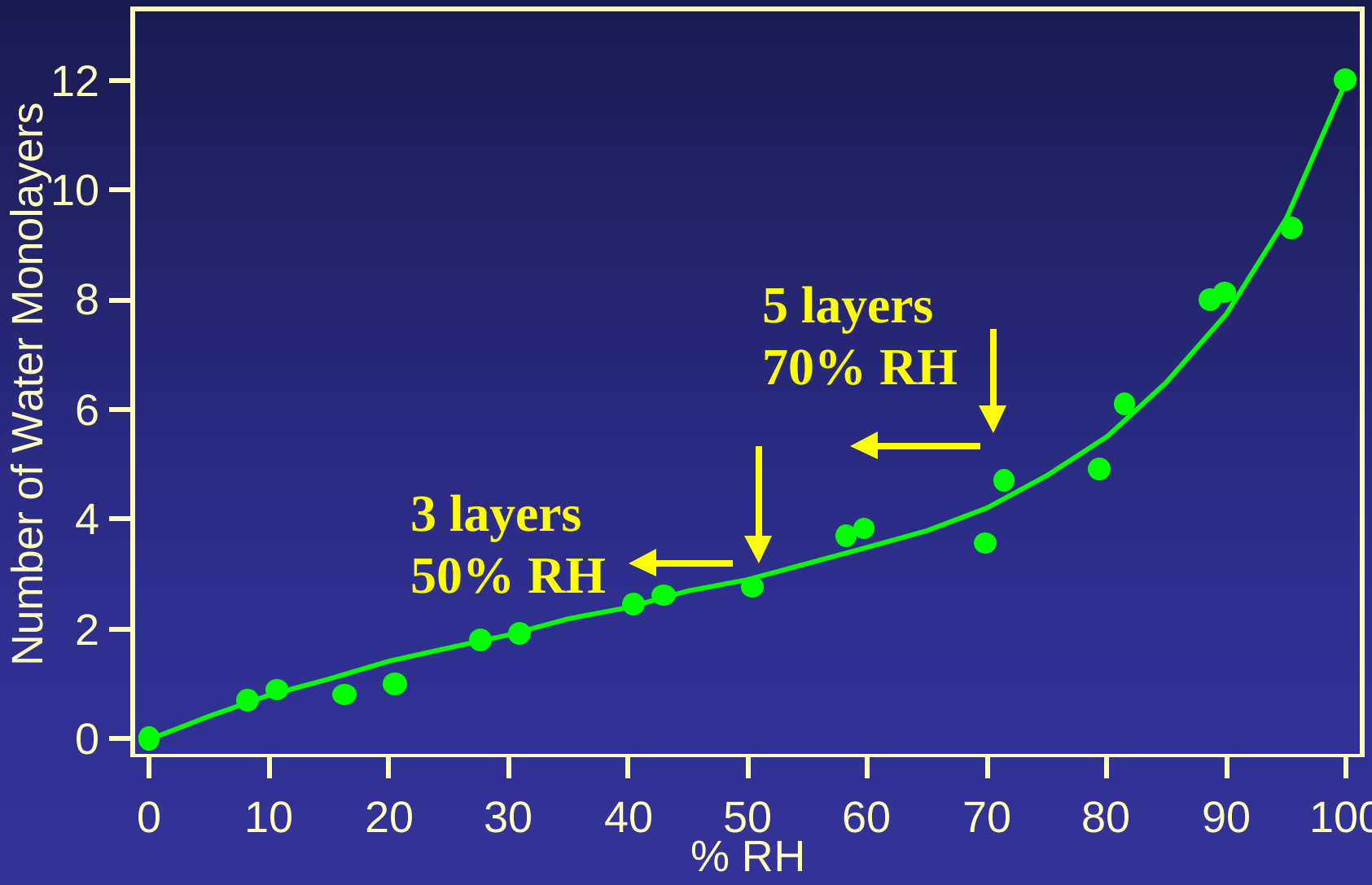


- Measure surface water by strong IR band at 3400 cm^{-1}

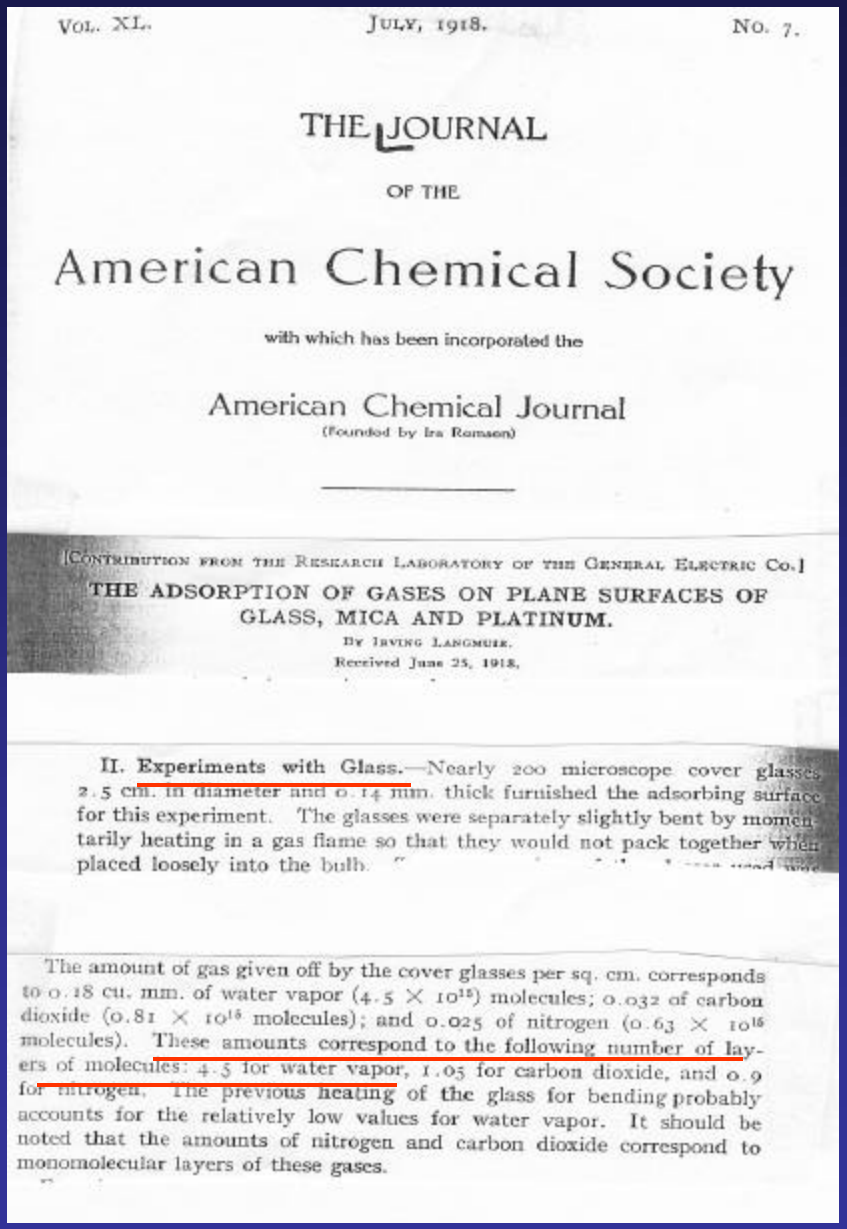
UPTAKE OF H_2O ON GLASS



NUMBER OF WATER LAYERS ON GLASS



COMPARISON TO LITERATURE



VOL. XL. JULY, 1918. NO. 7.

THE JOURNAL

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American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM.

BY IRVING LANGMUIR.

Received June 25, 1918.

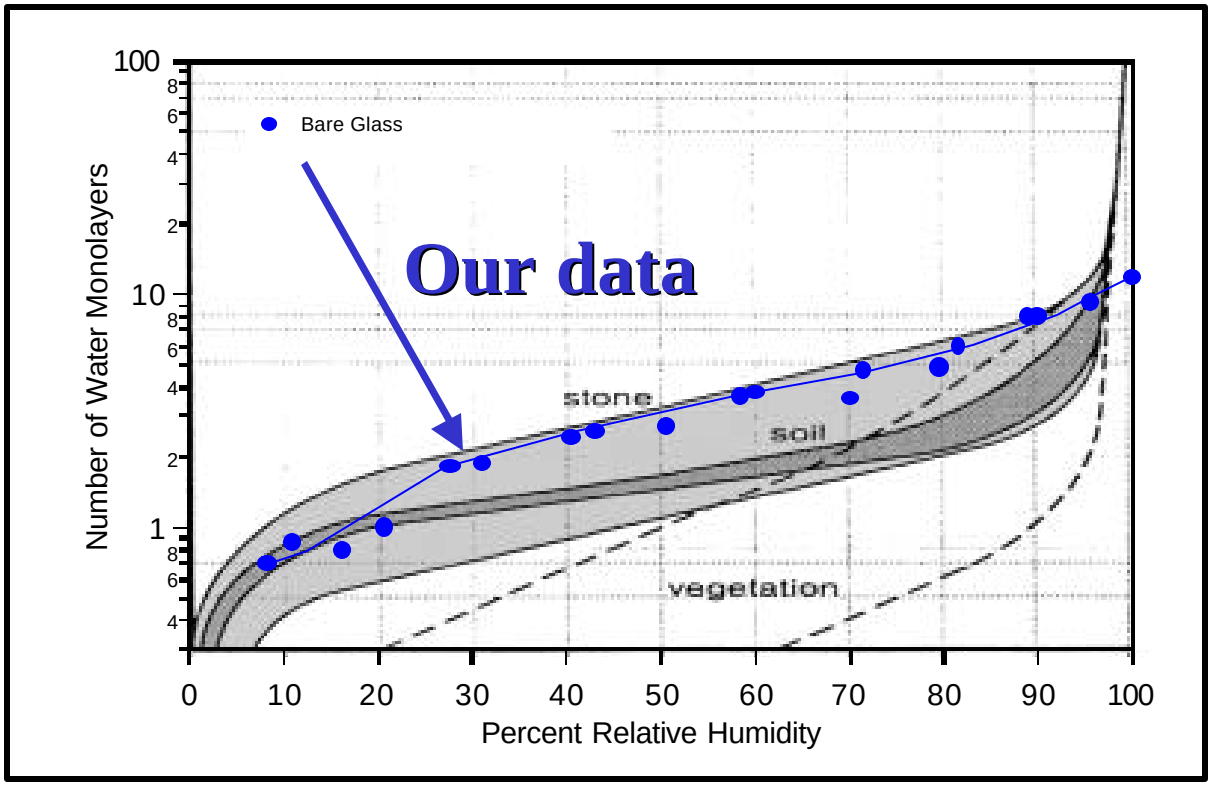
II. **Experiments with Glass.**—Nearly 200 microscope cover glasses 2.5 cm. in diameter and 0.14 mm. thick furnished the adsorbing surface for this experiment. The glasses were separately slightly bent by momentarily heating in a gas flame so that they would not pack together when placed loosely into the bulb.

The amount of gas given off by the cover glasses per sq. cm. corresponds to 0.18 cu. mm. of water vapor (4.5×10^{15}) molecules; 0.032 of carbon dioxide (0.81×10^{15} molecules); and 0.025 of nitrogen (0.63×10^{15} molecules). These amounts correspond to the following number of layers of molecules: 4.5 for water vapor, 1.05 for carbon dioxide, and 0.9 for nitrogen. The previous heating of the glass for bending probably accounts for the relatively low values for water vapor. It should be noted that the amounts of nitrogen and carbon dioxide correspond to monomolecular layers of these gases.

SURFACES AVAILABLE FOR HETEROGENEOUS REACTIONS

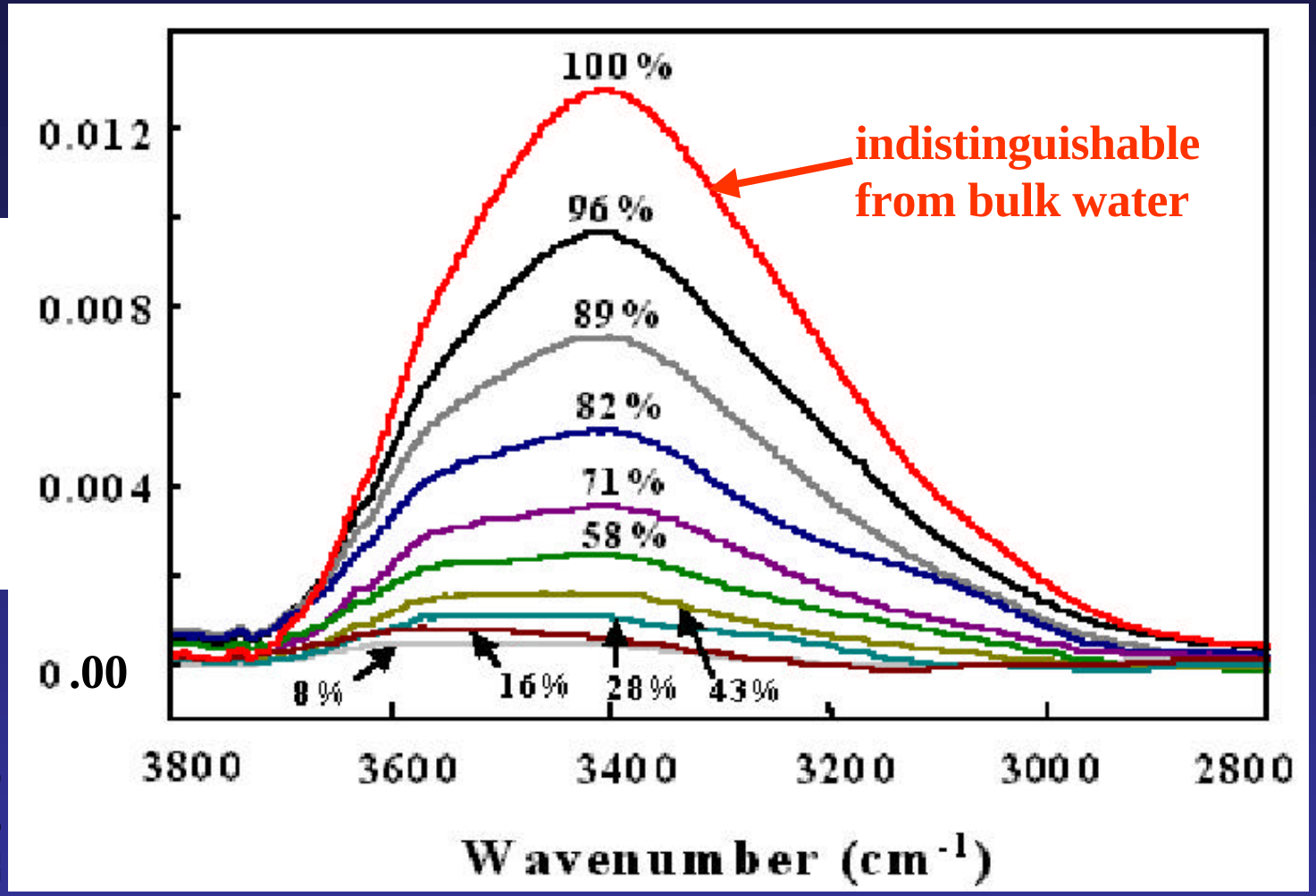
WATER UPTAKE ON ENVIROMENTAL SURFACES

Water Uptake on Glass Compared with Ambient Surfaces



G. Lammel, Formation of Nitrous Acid: Parameterisation and Comparison with Observations, Report No. 286, Max-Planck-Institut Für Meteorologie, Hamburg, 1999.

IS IT "BULK" WATER?



- Shift in band peak to higher wavenumbers (higher energy) ® "2 D" water!

KEY POINT #1

- **Cannot treat chemistry as uptake into bulk water film on surface, followed by "conventional" aqueous phase reactions**

-chemistry in 2-D!

SO WHAT??

- **Affects nature of species on surface, their reactivity and kinetics, i.e. entire reaction!**

e.g., HNO_3, NO_2/N_2O_4

WHY IS HNO_3 NOT SEEN AS A PRODUCT IN GAS PHASE?

- Stays “stuck” to surface????

- Why???

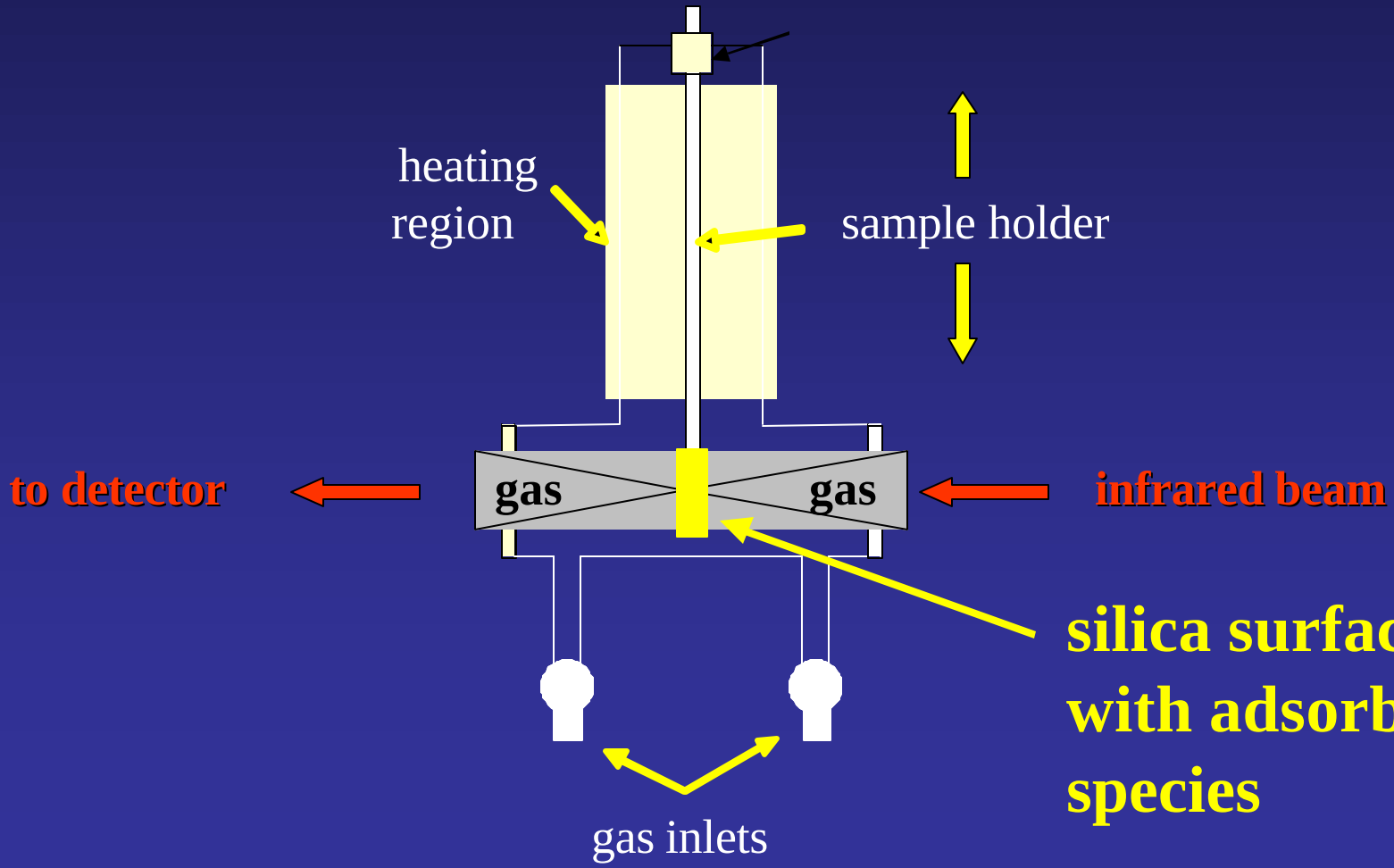
  -HNO_3 has high vapor pressure!

SILICA SAMPLES USED TO STUDY SURFACE REACTIONS

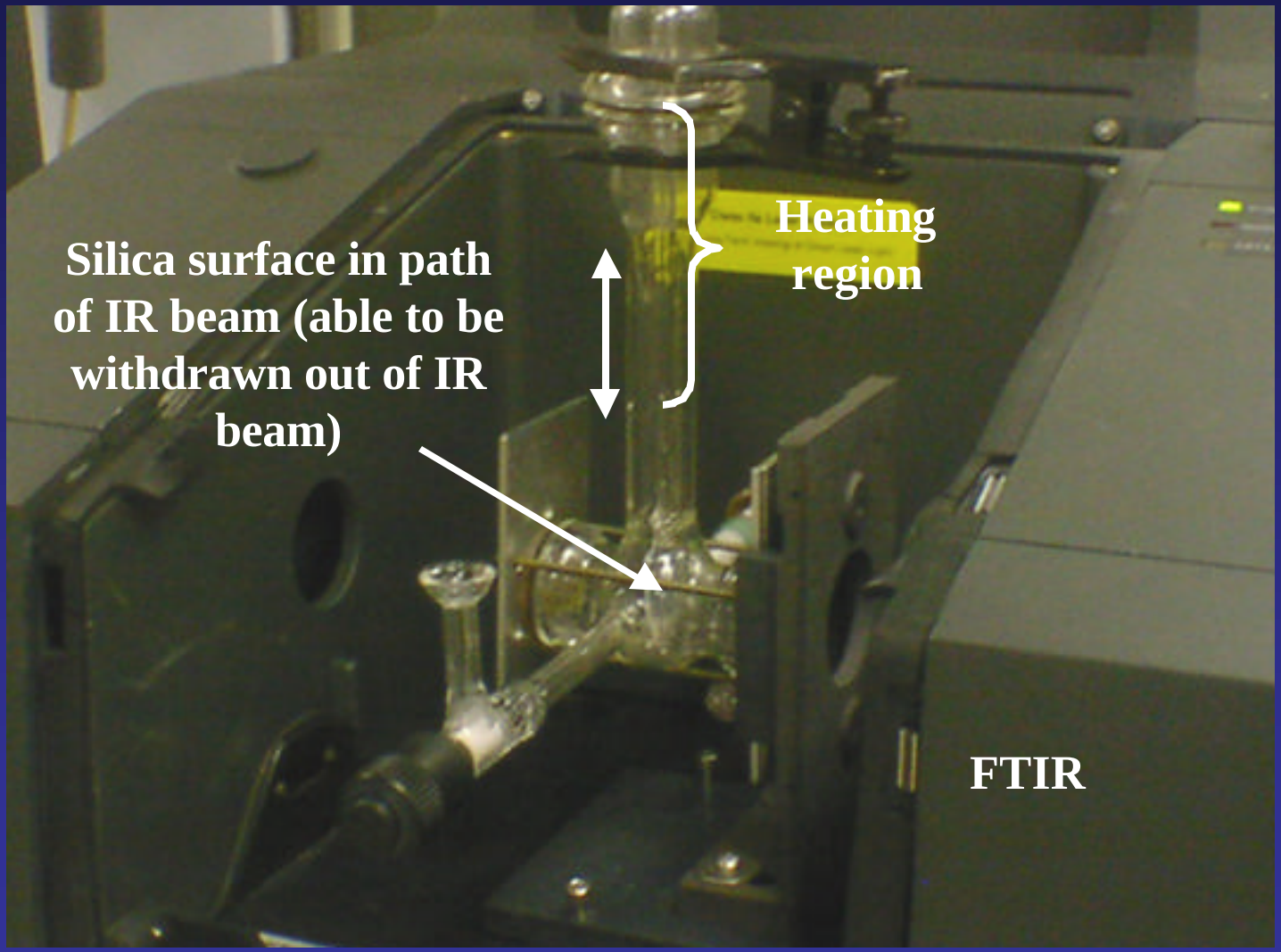
← silica powder & pressed disc

← porous glass (etched)

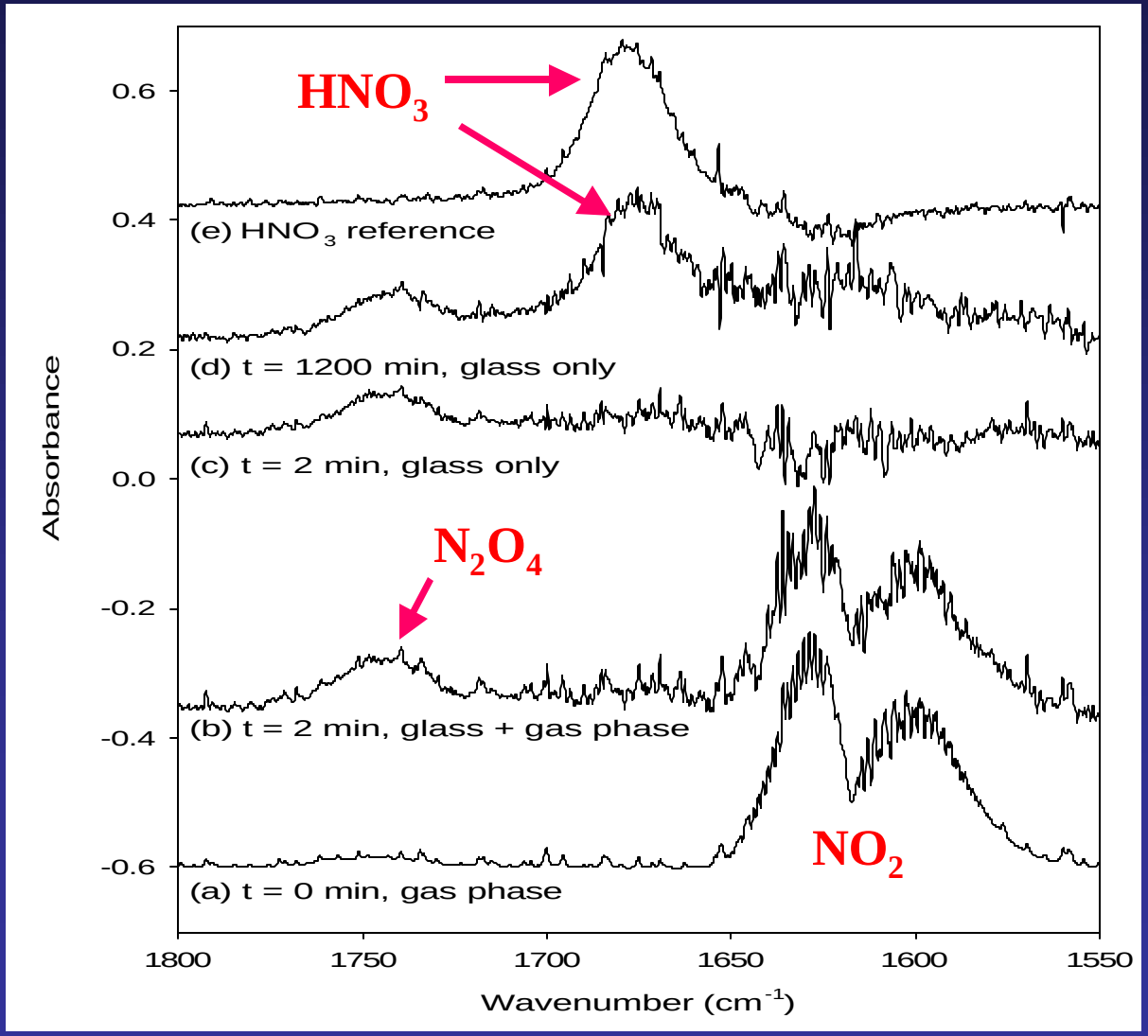
CELL USED TO STUDY CHEMISTRY ON SILICA SURFACES



POROUS GLASS CELL



FORMATION OF HNO_3 (AND N_2O_4) ON SURFACE



Add NO_2 to cell with "wet" porous glass

- HNO_3 is formed & stays on surface

- N_2O_4 enhanced on surface ® key intermediate?

KEY POINT #2

- **HNO_3 is the second product!**

- **HNO_3 stays on surface meshed with "2-D" water**

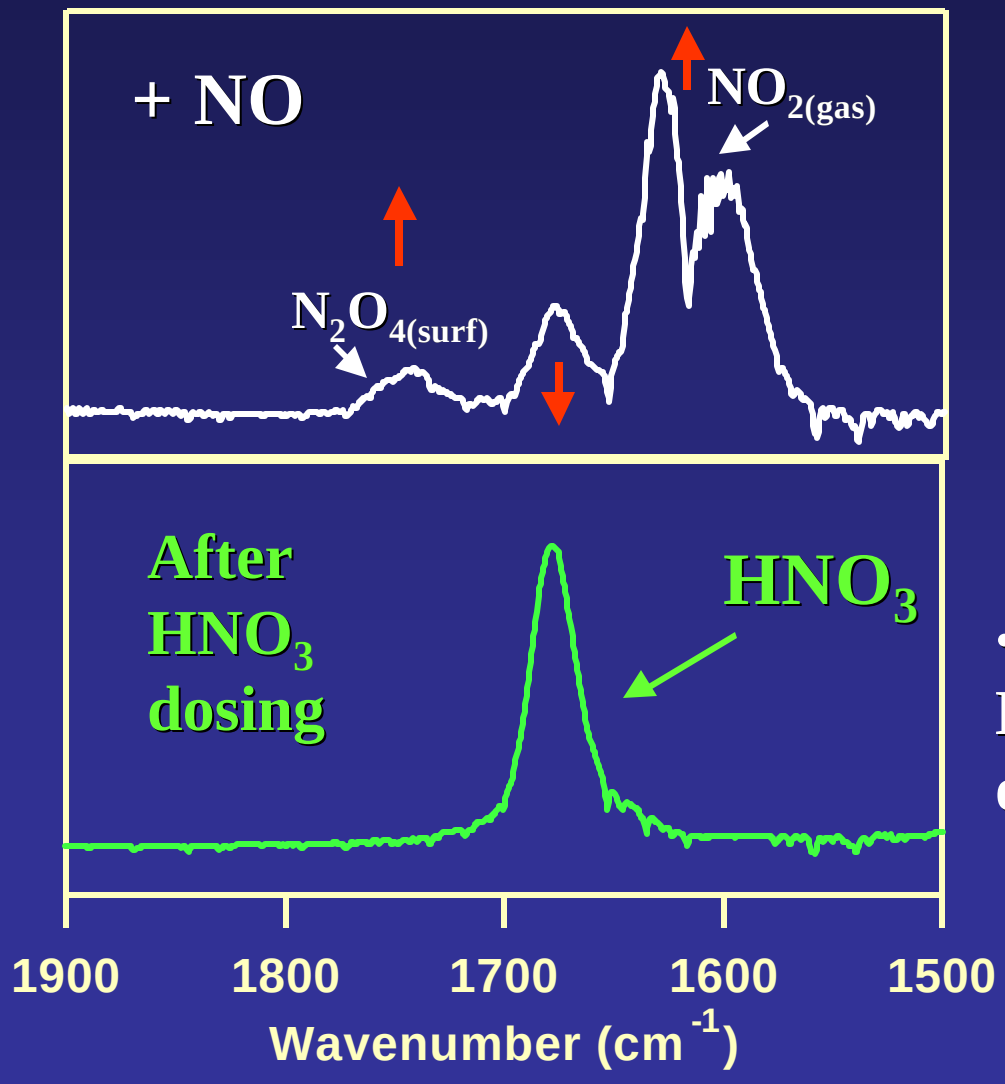
- **At least part of the HNO_3 is undissociated ® effect of 2-D water?**

SO WHAT??

- **Undissociated HNO_3 undergoes some unique reactions to regenerate NO_x**

Maybe HNO_3 is not "end of the line"?
-implications for control strategies

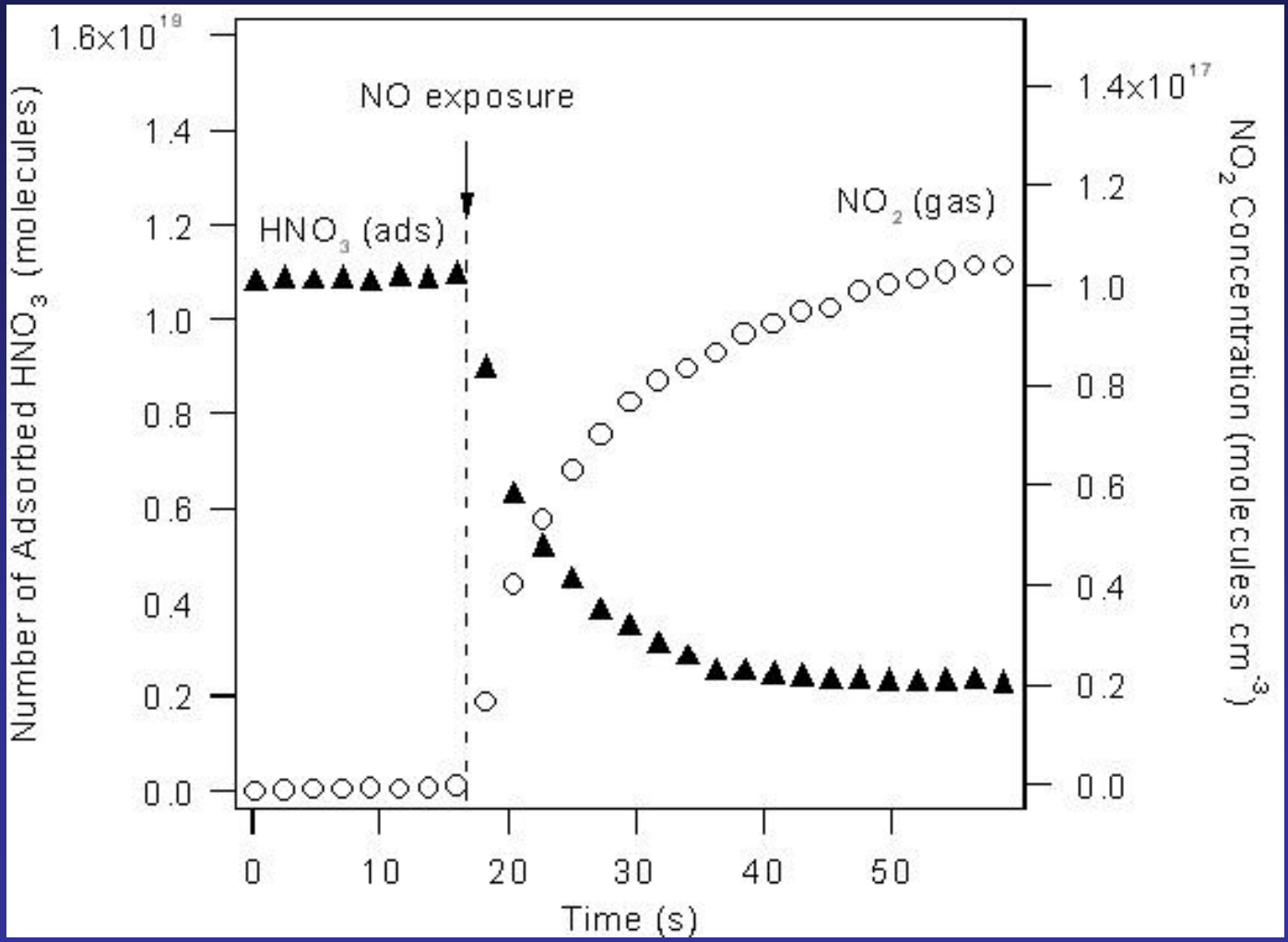
REACTION OF NO WITH HNO_3 ON POROUS GLASS



- NO reacts with $HNO_{3(surf)}$ to give NO_2

- undissociated HNO_3 "sticks" on surface

CONVERSION OF SURFACE HNO_3 TO NO_2



MECHANISM OF NO REACTION WITH SURFACE HNO_3

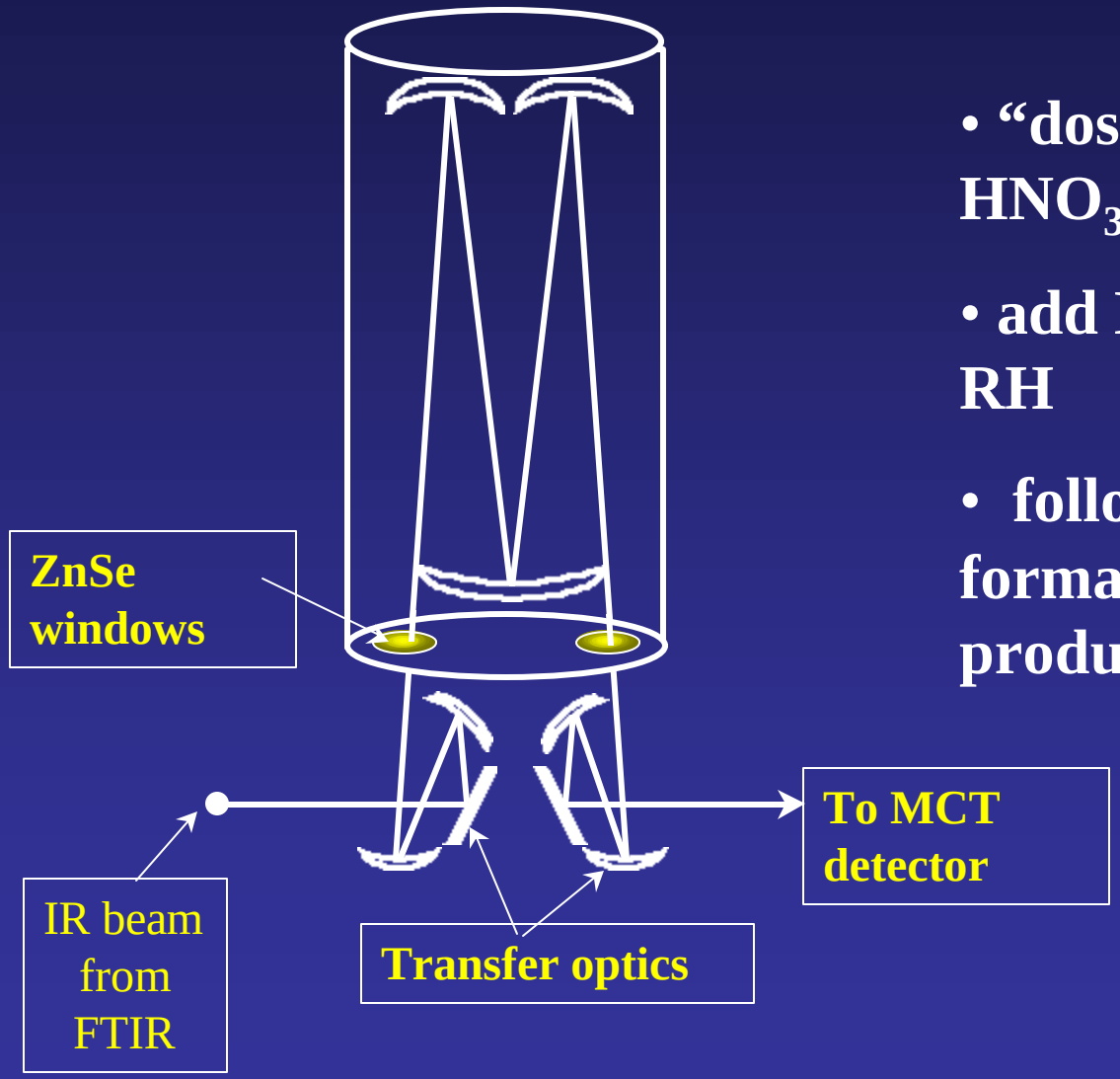
$$HNO_3 + NO \rightarrow HONO + NO_2$$

$$HONO + HNO_3 \rightarrow 2\,NO_2 + H_2O$$

NET:

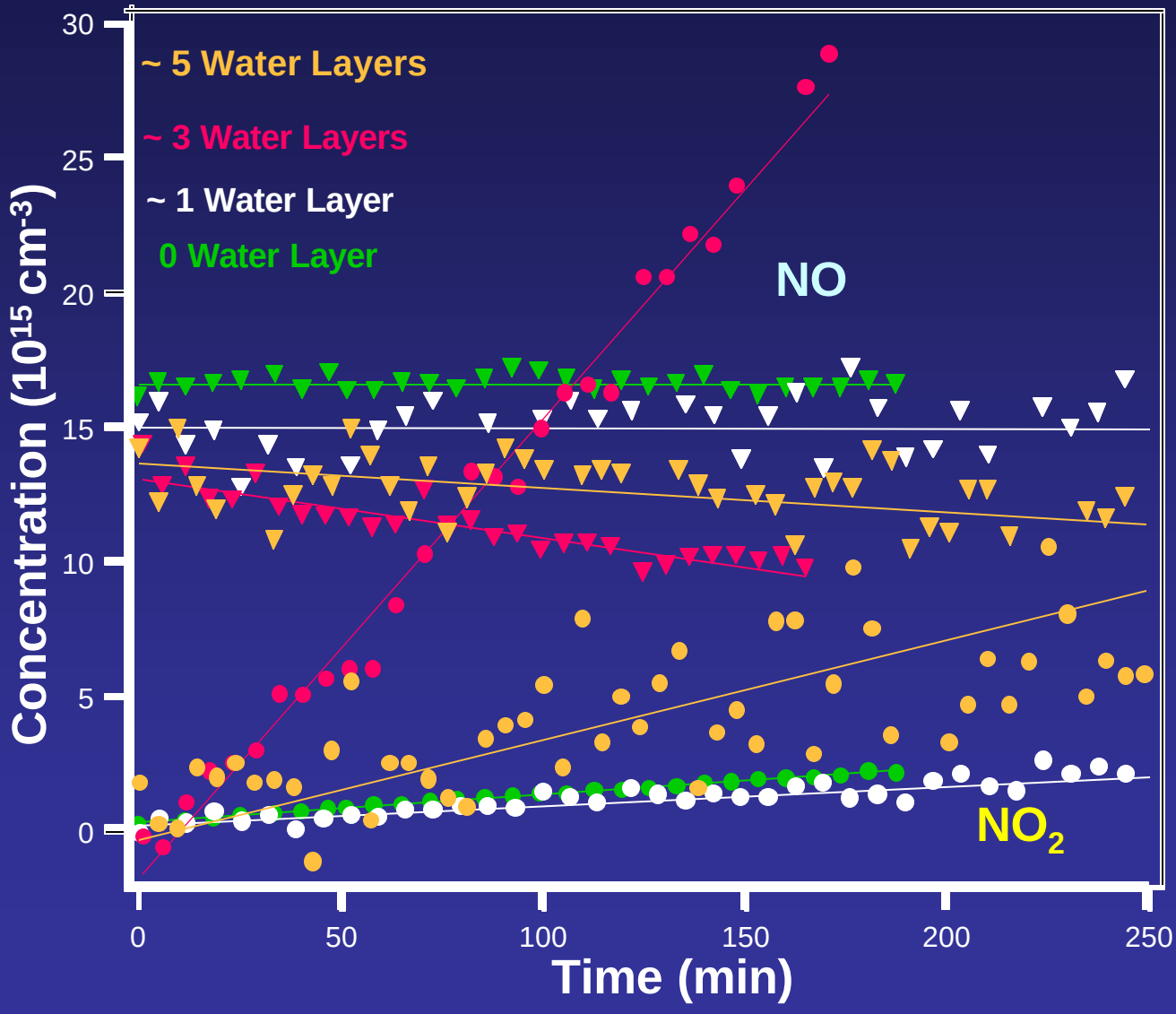
$$2\,HNO_3 + NO \rightarrow 3\,NO_2 + H_2O$$

REACTION OF NO WITH HNO_3 ON GLASS CELL SURFACE



- "dose" cell with gaseous HNO_3 and pump out
- add NO in N_2 at chosen RH
- follow loss of NO and formation of gaseous products

REACTION OF NO WITH HNO_3 ON A SMOOTH GLASS CELL WALL



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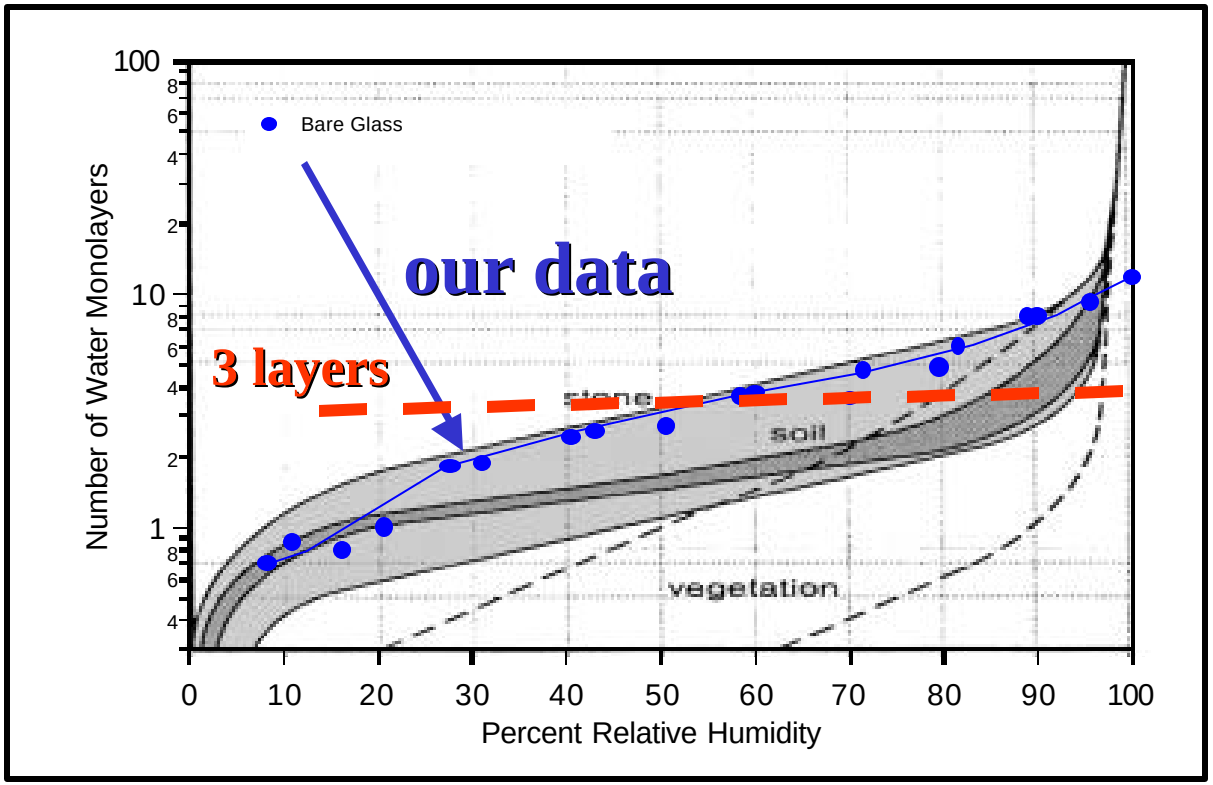

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REACTION OF NO WITH SURFACE HNO_3 ON SMOOTH GLASS SURFACE

- Reaction slower with 2 layers or $\geq$ 5 layers of water

$\geq$ 5 layers: $HNO_3 \rightarrow H^+ + NO_3^-$

-undissociated HNO_3 is key to reaction?

1 -2 layers??

THERMOCHEMISTRY OF NO REACTION WITH HNO_3

$$HNO_3 + NO \rightarrow HONO + NO_2$$

All gases: $\Delta H^0 = -0.3$ kcal mol^{-1}

$$HONO + HNO_3 \rightarrow 2\,NO_2 + H_2O$$

All gases: $\Delta H^0 = +9.3$ kcal mol^{-1}

NET:

$$2\,HNO_3 + NO \rightarrow 3\,NO_2 + H_2O$$

All gases: $\Delta H^0 = +9$ kcal mol^{-1}

THERMOCHEMISTRY OF SURFACE HNO_3 REACTIONS

ΔH^{298} (kcal mol^{-1})

$HONO_{(g)} + HNO_{3(g)} \rightarrow 2\,NO_{2(g)} + H_2O_{(g)}$ + 9.3

-10 -7.2 -21 -10.5

$HONO_{(hydr)}$ $HNO_{3(hydr)}$ $N_2O_{4(hydr)}$ $H_2O_{(l)}$

~ - 5

ROLE OF WATER ON SURFACE

- "2-D" water means at least some of HNO_3 is undissociated ® unique chemistry & renoxification

- water "solvates" reactants and products ® makes reactions exothermic

≤ 2 layers of water insufficient for "solvation" ?

SO WHAT??

- **Likely that under atmospheric conditions, some of deposited HNO_3 can be converted back into NO_x**

OVERALL NO_2 HYDROLYSIS REACTION

(and other heterogeneous chemistry)

"surface"

$$2\,NO_2 + H_2O \longrightarrow HONO + HNO_3$$

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